

## Azide-alkyne click approach to the preparation of dendrimer-type multi(thia)calix[4]arenes with triazole linkers

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### Abstract

© ISUCT Publishing. The design of polymacrocyclic structures is of high importance for the improvement of recognition ability to various guests. We present a convenient approach towards two types of dendrimer-shaped pentakis-thiacalix[4]arenes with triazolyl linkers using the click reaction of tetraazidoalkoxycalixarenes with monoalkynyloxy derivatives, as well as tetraalkynyloxyalixarenes with monoazidoalkoxy derivatives. Mitsunobu alkylation of hydroxyl groups has been employed to afford tetrasubstituted derivatives in 1,3-alternate configuration. A facile procedure for the synthesis of monosubstituted cone precursors in high yields by the hydrolysis of one ether fragment in disubstituted counterparts under basic conditions (n-BuNH<sub>2</sub> or NaN<sub>3</sub> in DMF) has been suggested and optimized. CuAAC reaction has been conducted in microwave reactor and on a hot plate. It has been found that microwave irradiation promotes the reaction and the yields of products are as high as 40–80 %.

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### Keywords

Azide-alkyne cycloaddition, Microwave irradiation, Multicalixarenes, Triazoles

### References

- [1] Designing Dendrimers (Campagna S., Ceroni P., Puntoriero F., Eds.) Hoboken: Wiley, 2011. 616 p.
- [2] Astruc D., Boisselier E., Ornelas C. Chem. Rev. 2010, 110, 1857–1959
- [3] Dendrimers, Dendrons, and Dendritic Polymers (Tomalia D.A., Christensen J.B., Boas U., Eds.) Cambridge: Cambridge Univ. Press, 2012. 412 p.
- [4] Calixarenes. An Introduction (Gutsche C.D., Ed.) Cambridge: Royal Society of Chemistry, 2008. 276 p.
- [5] Morohashi N., Narumi F., Iki N., Hattori T., Miyano S. Chem. Rev. 2006, 106, 5291–5316
- [6] Konovalov A.I., Antipin I.S. Mendeleev Commun. 2008, 18, 229–237
- [7] Kumar R., Lee Y.O., Bhalla V., Kumar M., Kim J.S. Chem. Soc. Rev. 2014, 43, 4824–4870
- [8] Muravev A.A., Burilov V.A., Solov'eva S.E., Strel'nik A.G., Latypov S.K., Bazanova O.B., Sharafutdinova D.R., Antipin I.S., Konovalov A.I. Russ. Chem. Bull. 2014, 63, 214.
- [9] Rudzevich Y., Fischer K., Schmidt M., Böhmer V. Org. Biomol. Chem. 2005, 3, 3916–3925.
- [10] Rotan O., Sokolova V., Gilles P., Hu W., Dutt S., Schrader T., Epple M. Mat.-wiss. u. Werkstofftech. 2013, 44, 176–182.
- [11] Lalor R., DiGesso J.L., Mueller A., Matthews S.E. Chem. Commun. 2007, 46, 4907–4909

- [12] Lu Y., Xiao C., Yu Z., Zeng X., Ren Y., Li C. J. *Mater. Chem.* 2009, 19, 8796–8802.
- [13] Jiansen L., Zhenlin Z., Yuanyin C., Xueran L. *Tetrahedron Lett.* 1998, 39, 6507–6510
- [14] Tilki T., Şener I., Karci F., Gülce A., Deligöz H. *Tetrahedron* 2005, 61, 9624–9629
- [15] Bhalla V., Nagendra Babu J., Kumar M., Hattori T., Miyano S. *Tetrahedron Lett.* 2007, 48, 1581–1585.
- [16] Hamdi A., Lee Y.H., Kim Y., Kusumahastuti D.K.A., Ohto K., Abidi R., Vicens J. *Tetrahedron Lett.* 2009, 50, 540–543.
- [17] Csokai V., Balázs B., Tóth G., Horváth G., Bitter I. *Tetrahedron* 2004, 60, 12059–12066
- [18] Khomich E., Kashapov M., Vatsouro I., Shokova E., Kovalev V. *Org. Biomol. Chem.* 2006, 4, 1555–1560
- [19] Kim S.K., Sim W., Vicens J., Kim J.S. *Tetrahedron Lett.* 2003, 44, 805–809
- [20] Muravev A.A., Galieva F.B., Bazanova O.B., Sharafutdinova D.R., Solovieva S.E., Antipin I.S., Konovalov A.I. *Supramol. Chem.* 2016, 28, 589–600.
- [21] Pappalardo A., Ballistreri F.P., Li Destri G., Mineo P.G., Tomaselli G.A., Toscano R.M., Sfrazzetto G.T. *Macromolecules* 2012, 45, 7549–7556
- [22] Wiktorowicz S., Aseyev V., Tenhu H. *Polym. Chem.* 2012, 3, 1126–1129
- [23] Prata J.V., Costa A.I., Pescitelli G., Pinto H.D. *Polym. Chem.* 2014, 5, 5793–5803.
- [24] Galán H., Teresa Murillo M., Quesada R., Escudero-Adán E.C., Benet-Buchholz J., Prados P., de Mendoza J. *Chem. Commun.* 2010, 46, 1044–1046
- [25] Feng J., Liu K., Li Y., Yang M. *Polym. Adv. Technol.* 2009, 20, 514–518
- [26] Gattuso G., Grasso G., Marino N., Notti A., Pappalardo A., Pappalardo S., Parisi M.F. *Eur. J. Org. Chem.* 2011, 5696–5703
- [27] Lalor R., Gunning A.P., Morris V.J., Matthews S.E. *Chem. Commun.* 2010, 46, 8665–8667
- [28] Bu J.-H., Zheng Q.-Y., Chen C.-F., Huang Z.-T. *Tetrahedron* 2005, 61, 897–902
- [29] Wang J., Gutsche C.D. *J. Org. Chem.* 2002, 67, 4423–4429
- [30] Szemes F., Drew M.G.B., Beer P.D. *Chem. Commun.* 2002, 1228–1229
- [31] Stastny V., Stibor I., Dvorakova H., Lhotak P. *Tetrahedron* 2004, 60, 3383–3391.
- [32] Fischer C., Weber E. J. *Incl. Phenom. Macrocycl. Chem.* 2014, 79, 151–160
- [33] Morales-Sanfrutos J., Ortega-Muñoz M., Lopez-Jaramillo J., Hernandez-Mateo F., Santoyo-Gonzalez F. *J. Org. Chem.* 2008, 73, 7768–7771
- [34] Hwang G.T., Kim B.H. *Tetrahedron* 2002, 58, 9019–9028.
- [35] Li H., Zhan J., Chen M., Tian D., Zou Z. *J. Incl. Phenom. Macrocycl. Chem.* 2010, 66, 43–47
- [36] Wang N.J., Sun C.M., Chung W.S. *Sens. Actuators, B* 2012, 171–172, 984–993
- [37] Cecioni S., Lalor R., Blanchard B., Praly J.P., Imberty A., Matthews S.E., Vidal S. *Chem. Eur. J.* 2009, 15, 13232–13240.
- [38] *Purification of Laboratory Chemicals* (Armarego W.L.F., Chai C.L.L., Eds.) Oxford: Butterworth-Heinemann, 2009. 760 p.
- [39] Tyuftin A.A., Solovieva S.E., Murav'ev A.A., Polyantsev F.M., Latypov Sh.K., Antipin I.S. *Russ. Chem. Bull.* 2009, 58, 145–151.
- [40] Bitter I., Csokai V. *Tetrahedron Lett.* 2003, 44, 2261–2265
- [41] Muravev A.A., Galieva F.B., Strel'nik A.G., Nugmanov R.I., Gruner M., Solov'eva S.E., Latypov Sh.K., Antipin I.S., Konovalov A.I. *Russ. J. Org. Chem.* 2015, 51, 1334–1342.
- [42] Solov'eva S.E., Murav'ev A.A., Latypov Sh.K., Antipin I.S., Konovalov A.I. *Dokl. Chem.* 2011, 438, 170–174.
- [43] Akdas H., Bringel L., Bulach V., Graf E., Hosseini M.W., De Cian A. *Tetrahedron Lett.* 2002, 43, 8975–8979.
- [44] Lang J., Vlach J., Dvorakova H., Lhotak P., Himl M., Harbal R., Stibor I. *J. Chem. Soc., Perkin Trans. 2* 2001, 576–580.
- [45] Buriilov V.A., Ibragimova R.R., Nugmanov R.I., Sitdikov R.R., Islamov D.R., Kataeva O.N., Solov'eva S.E., Antipin I.S. *Russ. Chem. Bull.* 2015, 64, 2114–2124.
- [46] Buriilov V.A., Nugmanov R.I., Ibragimova R.R., Solovieva S.E., Antipin I.S. *Mendeleev Commun.* 2015, 25, 177–179.
- [47] Lavendomme R., Leroy A., Luhmer M., Jabin I. *J. Org. Chem.* 2014, 79, 6563–6570.
- [48] Lavendomme R., Zahim S., De Leener G., Inthasot A., Mattiuzzi A., Luhmer M., Reinaud O., Jabin I. *Asian J. Org. Chem.* 2015, 4, 710–722.
- [49] Matsumiya H., Terazono Y., Iki N., Miyano S. *J. Chem. Soc., Perkin Trans. 2* 2002, 1166–1172.
- [50] Omran O.A. *Heterocycles* 2016, 92, 1085–1094
- [51] Kasyan O., Healey E.R., Drapailo A., Zaworotko M., Cecillon S., Coleman A.W., Kalchenko V. *J. Incl. Phenom. Macrocycl. Chem.* 2007, 58, 127–132

- [52] Galukhin A.V., Zaikov E.N., Antipin I.S., Konovalov A.I., Stoikov I.I. *Macroheterocycles* 2012, 5, 266–274
- [53] Stoikov I.I., Ibragimova D.S., Shestakova N.V., Krivolapov D.B., Litvinov I.A., Antipin I.S., Konovalov A.I., Zharov I. *Supramol. Chem.* 2009, 21, 564–571
- [54] Nosov R.V., Stoikov I.I. *Macroheterocycles* 2015, 8, 120–127
- [55] Dvořáková H., Lang J., Vlach J., Sýkora J., Čajan M., Himl M., Pojarová M., Stibor I., Lhoták P. *J. Org. Chem.* 2007, 72, 7157–7166.
- [56] Solovieva S.E., Muravev A.A., Zakirzyanov R.T., Latypov S.K., Antipin I.S., Konovalov A.I. *Macroheterocycles* 2012, 5, 17–22
- [57] Muravev A.A., Solovieva S.E., Latypov S.K., Antipin I.S., Konovalov A.I. *Phosphorus, Sulfur Silicon Relat. Elem.* 2013, 188, 499–502
- [58] Muravev A.A., Solovieva S.E., Kochetkov E.N., Mel'nikova N.B., Safiullin R.A., Kadirov M.K., Latypov S.K., Antipin I.S., Konovalov A.I. *Macroheterocycles* 2013, 6, 302–307.
- [59] Lamouchi M., Jeanneau E., Chiriac R., Ceroni D., Meganem F., Brioude A., Coleman A.W., Desroches C. *Tetrahedron Lett.* 2012, 53, 2088–2090.
- [60] Solovieva S.E., Popova E.V., Omran A.O., Gubaidullin A.T., Kharlamov S.V., Latypov Sh.K., Antipin I.S., Konovalov A.I. *Russ. Chem. Bull.* 2011, 60, 486–498.
- [61] Nakamura Y., Tanaka S., Serizawa R., Morohashi N., Hattori T. *J. Org. Chem.* 2011, 76, 2168–2179.
- [62] Latypov S., Epifanova N., Popova E., Vasilevsky S., Solovieva S., Antipin I., Konovalov A. *Appl. Magn. Reson.* 2011, 41, 467–475.